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STRUCTURAL INTERPRETATION OF CONCENTRATION DEPENDENCES OF GLASS MOLAR VOLUME IN SYSTEMS $R_2O - R'_2O - SiO_2$, $RO - R'O - SiO_2$, and $R_2O - RO - SiO_2$

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The method for structural interpretation of concentration dependences of properties of binary silicate systems based on establishing a correlation between the values of a considered parameter and the degree of depolymerization of the glass structural lattice is completely applicable in the case of ternary silicate glasses containing modifying oxides of the first and second groups of the periodic system in various combinations (the usual estimation error for glass molar volume is ~ 1%). It is shown that the effect of the interaction between various modifying oxides on variations in glass properties is insignificant or absent.

We earlier [1] proposed a method for structural interpretation of concentration dependences of properties in binary silicate glasses (using the example of glass molar volume) based on establishing a correlation between the values of a certain considered property and the degree of depolymerization of the silicon-oxygen skeleton (structural lattice) of glass R^* reflected in the number of non-bridge oxygen ions per silicon-oxygen tetrahedron. In doing so, we established partial values of molar volume for a number of modifying oxides of the I and II groups of the periodic system of elements (Table 1) proportional to the cube of the modifying oxide cation radius and retaining their constant values over the whole vitrification field. The estimation error of the glass molar volume in using the specified partial coefficients was ~ 1%.

The calculation of the molar volume of glass is performed according to the equation approximating the dependence of the molar volume V_m (cm^3/mole) on the degree of depolymerization of the glass structural lattice R^* [1]:

$$V_m = 27.29 + k_{1j} R^* + k_{2j} R^{*2}, \quad (1)$$

where 27.29 is the molar volume of vitreous silica, cm^3/mole, calculated from the density value of 2.202 g/cm^3 (the averaged value from[2]), and k_{1j} and k_{2j} are partial coefficients of modifier oxides (Table 1).

For binary glasses, the value of R^* is estimated from the expression [1]

$$R^* = x/2(1-x), \quad (2)$$

where x is the molar part of the modifying oxide.

The present paper describes the verification of the applicability of the method in [1] for approximation of the concentration dependences of properties of ternary silicate glasses containing modifying oxides of the first and second groups of the periodic system in different combinations.

The study included analysis of dependences of the molar volume V_m on the depolymerization degree of the structural lattice R^* in ternary silicate glasses of the systems $R_2O - R'_2O - SiO_2$, $RO - R'O - SiO_2$, and $R_2O - RO - SiO_2$ based on experimental data on the density of various glasses supplied by different authors.

The glass molar volume V_m was calculated from the formula [3]

$$V_m = M_m/\rho = \Sigma m_{mi} x_i/\rho,$$

where M_m is glass molar mass, g/mole, ρ is the glass density, g/cm^3, m_{mi} are the molar masses of oxides, g, and x_i are the molar parts of oxides.

In passing from estimating the properties of binary glasses to the calculation of multicomponent glass properties, in particular, ternary glasses, the form of calculation equations (1) and (2) is somewhat modified, although their physical meaning remains the same, that is:

the depolymerization degree of the glass structural lattice R^* is calculated according to the expression

$$R^* = \frac{\sum x_j}{2(1-\sum x_j)}, \quad (3)$$

where x_j are the molar parts of modifying oxides;

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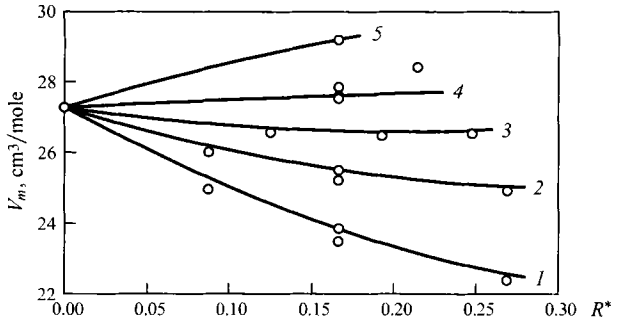

Fig. 1. Concentration dependence of glass molar volume for glasses of the $R_2O - R'_2O - SiO_2$ system. R_2O, R'_2O: Li_2O, Na_2O (*1*); Li_2O, K_2O (*2*); Na_2O, K_2O (*3*); Na_2O, Rb_2O (*4*); K_2O, Rb_2O (*5*). Solid lines) estimated values; dots) experimental data from various authors (Table 2).

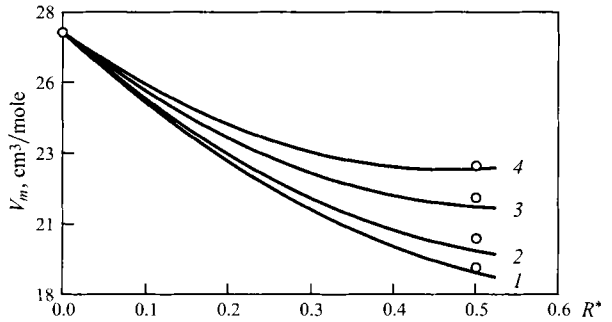

Fig. 2. Concentration dependence of glass molar volume for glasses of the $R_2O - R'O - SiO_2$ system illustrated by the example of glass compositions $0.25RO \cdot 0.25R' \cdot 0.50SiO_2$. R_2O, R'2O: MgO, Ca_2O (*1*); MgO, SrO (*2*); MgO, BaO (*3*); CaO, BaO (*4*). Solid lines) estimated values; dots) experimental data from various authors (Table 3).

coefficients k_{ij} (Eq. (1)) become additive values depending on the ratio of the molar parts of modifying oxides:

$$k_1 = \sum k_{1j} \frac{x_j}{\sum x_j}; \quad (4)$$

$$k_2 = \sum k_{2j} \frac{x_j}{\sum x_j}. \quad (5)$$

The characteristics of the initial experimental data used in analysis of concentration dependences of glass molar volume in systems $R_2O - R'_2O - SiO_2$, as well as the values of the mean quadratic error in calculating V_m, are given in Table 2.

The results obtained completely substantiate the possibility of using the method in [1] to approximate concentration dependences of properties of ternary silicate glass systems containing modifying oxides of the first group of the periodic system in various combinations, which is proved by the high accuracy of the calculation of V_m (the relative mean quadratic error does not exceed 1%, Table 1) and the data in Fig. 1.

The characteristics of the reference experimental data used in the analysis of concentration dependences of the molar volume of glasses of the system $RO - R'O - SiO_2$, as

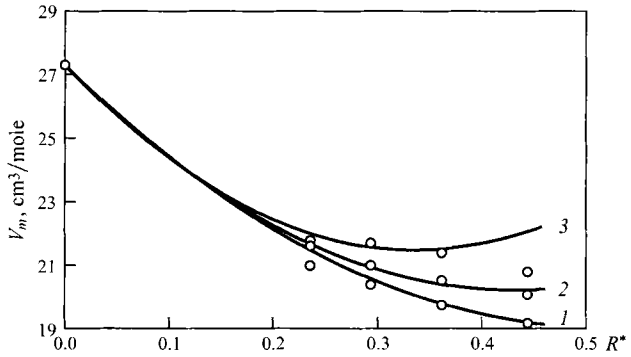

Fig. 3. Concentration dependence of glass molar volume for glasses of the $R_2O - RO - SiO_2$ system illustrated by the example of glass compositions $0.27\ Li_2O \cdot xRO \cdot (1 - 0.27 - x)SiO_2$. RO: MgO (*1*); CaO (*2*); BaO(*3*). Solid lines) estimated values; dots) experimental data from [4].

well as the mean quadratic error values for V_m calculation, are given in Table 3.

The results obtained also point to the possibility of using the method in [1] for approximation of concentration dependences of properties of ternary silicate glasses containing modifying oxides of the second group of the periodic table in different combinations (Table 3 and Fig. 2), although the calculation accuracy of V_m values is somewhat lower

TABLE 1

Modifying oxide	k_{1j}	k_{2j}
Li_2O	–33.9	39.4
Na_2O	–17.7	22.6
K_2O	4.5	7.5
Rb_2O	21.4	–22.0
MgO	–29.0	18.6
CaO	–24.5	20.3
SrO	–22.3	22.0
BaO	–16.9	23.9

TABLE 2

System	Relative mean quadratic error of V_m, %	Number of glass compositions used in data processing	Reference
$Li_2O - Na_2O - SiO_2$	0.54	19	[4]
$Li_2O - K_2O - SiO_2$	0.56	17	[4]
$Na_2O - K_2O - SiO_2$	0.24	45	[4*]
$Na_2O - Rb_2O - SiO_2$	0.86	10	[4, 5]
$K_2O - Rb_2O - SiO_2$	0.28	4	[4]

* Glass composition is determined by analysis.

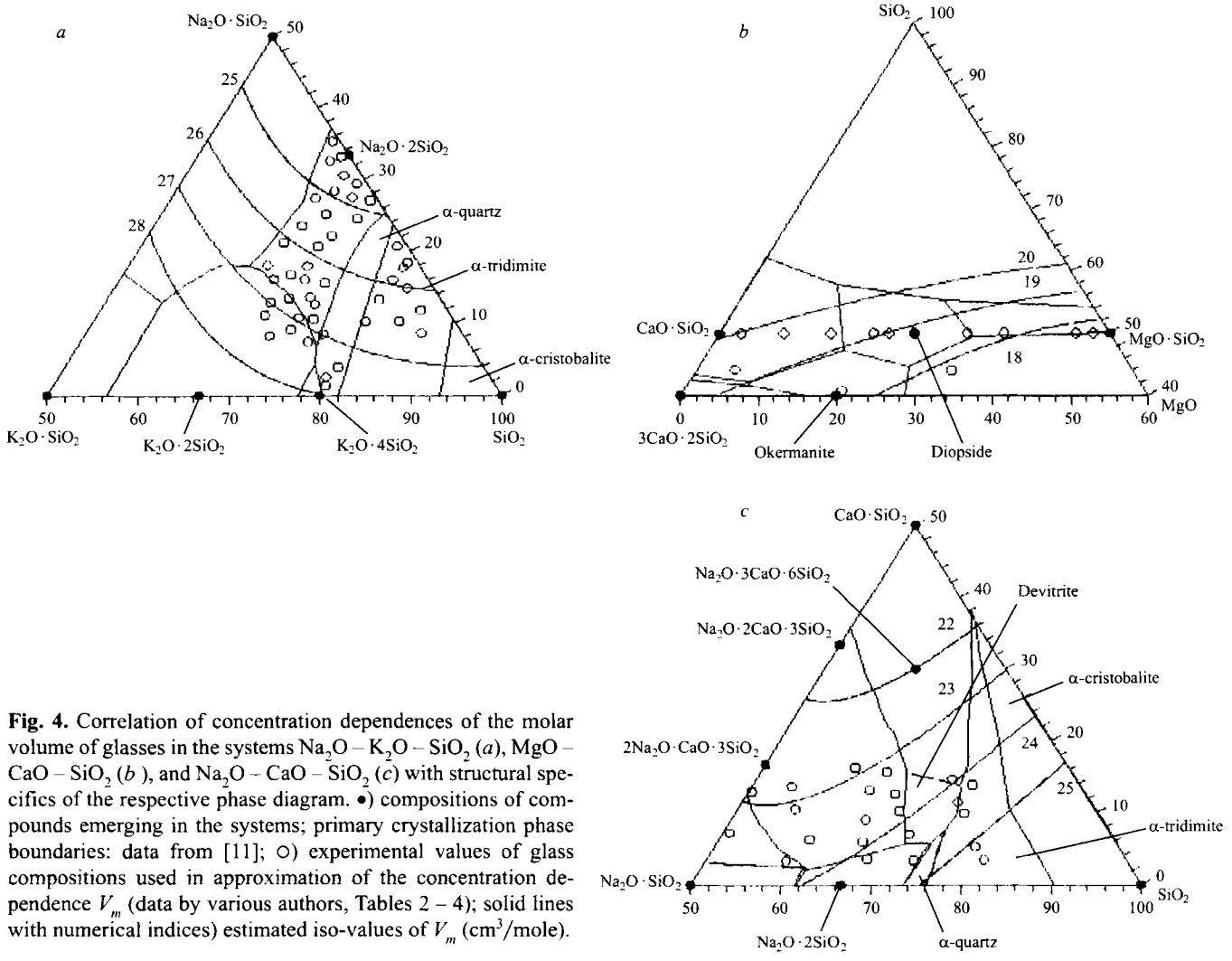

Fig. 4. Correlation of concentration dependences of the molar volume of glasses in the systems $Na_2O - K_2O - SiO_2$ (*a*), $MgO - CaO - SiO_2$ (*b*), and $Na_2O - CaO - SiO_2$ (*c*) with structural specifics of the respective phase diagram. •) compositions of compounds emerging in the systems; primary crystallization phase boundaries: data from [11]; ○) experimental values of glass compositions used in approximation of the concentration dependence V_m (data by various authors, Tables 2 – 4); solid lines with numerical indices) estimated iso-values of V_m (cm^3/mole).

than in the case of glasses of the $R_2O - R'_2O - SiO_2$ system, which can be due to the insufficient reliability of data on glass compositions published in the literature.

The characteristics of the reference experimental data used in the analysis of concentration dependences of the molar volume of glasses of the system $R_2O - RO - SiO_2$, as well as the mean quadratic error values for V_m calculation, are given in Table 4.

The results obtained in turn show the possibility of using the method in [1] for approximation of concentration dependences of properties of ternary silicate glasses containing modifying oxides of the first and second groups of the periodic system in different combinations (Table 4 and Fig. 3).

TABLE 3

System	Relative mean quadratic error of V_m, %	Number of glass compositions used in data processing	Reference
$MgO - CaO - SiO_2$	1.42	13	[4]
$MgO - SrO - SiO_2$	– 1.99*	2	[5]
$MgO - BaO - SiO_2$	0.77	2	[5]
$CaO - BaO - SiO_2$	0.86	2	[5]

* Relative mean arithmetic error.

TABLE 4

System	Relative mean quadratic error of V_m, %	Number of glass compositions used in data processing	Reference
$Li_2O - MgO - SiO_2$	+1.11*	4	[4]
$Li_2O - CaO - SiO_2$	0.22	4	[4]
$Li_2O - BaO - SiO_2$	+2.02*	4	[4]
$Na_2O - MgO - SiO_2$	2.42	46	[4**]
$Na_2O - CaO - SiO_2$	0.59	22	[4**]
$Na_2O - SrO - SiO_2$	+0.69*	9	[4**]
$Na_2O - BaO - SiO_2$	0.61	19	[4**, 4]
$K_2O - MgO - SiO_2$	1.64	13	[4**, 6]
$K_2O - CaO - SiO_2$	0.56	14	[4**, 6]
$K_2O - SrO - SiO_2$	1.03	57	[4**, 4]
$K_2O - BaO - SiO_2$	0.57	20	[4**, 6]

* Relative mean arithmetic error.

** Glass composition is determined by analysis.

The concentration dependences of the molar volume of ternary silicate glasses containing modifying oxides of the first and second groups of the periodic system (Figs. 1 – 3) show that their structural lattice, as a rule, becomes denser as their depolymerization progresses. The exceptions (the same as in the case of binary glasses of the $R_2O - SiO_2$ system [1]) are potassium and rubidium-containing glasses, in which the structural lattice is loosened (an increase in V_m, Fig. 1) with increasing degree of depolymerization, which is evidenced by a consistent decrease in the molar volume. The mechanism of such modification of molar volume in glasses is determined by the intensity of the variations in the values of partial coefficients k_{ij} which are part of Eq. (1) and a linear function of the cube of the radius of the modifier oxides [1].

The complete similarity in the concentration dependences of the molar volume of binary and ternary silicate glasses approximated by the method in [1] substantiates the assumption made in [7], i.e., that the effect of the reaction between various modifying oxides on the modification of glass properties is insignificant or not present at all. The latter suggests that the cations of various modifying oxides do not take preferential positions in the glass structural lattice and are statistically distributed over that lattice.

Equations (1) – (5) can be used to derive the equation which makes it possible to calculate ternary glass compositions with a preset constant value of molar volume, and based on these data to construct V_m isolines on the concentration triangle or the ternary phase diagram. The latter allows for a correlation between the concentration dependences of glass V_m and the structural specifics of respective phase diagrams.

Such calculations and constructions (using a specially developed computer program) were carried out in this study for glasses in the systems $Na_2O - K_2O - SiO_2$, $CaO - MgO - SiO_2$, and $Na_2O - CaO - SiO_2$. It was found (Fig. 4) that the concentration dependences of the molar volume of ternary glasses in the specified systems, the same as in the case of binary glass [1], are smoothly monotonic and do not exhibit abrupt bends while crossing the phase-field boundaries (primary crystallization fields) in the phase diagrams considered. This completely agrees with the conclusion drawn in [7] and shows that the approximation of concentration dependences of silicate glass properties suggested in some papers [8 – 10] based on fractional-linear functions correlated with phase diagram fields is in reality only a rough approximation.

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